

Application No. 10/076,976

REMARKS

Claims 18-30 are pending. Claims 18-30 stand as rejected, and Applicants respectfully request reconsideration of the rejections in based upon the comments below.

Rejections Under 35 U.S.C. § 112

The Examiner rejected claims 18-21, 23-28 and 30 under 35 U.S.C. § 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. Specifically, the Examiner asserted that "there is no support for 150 nm, 125 nm or 25 nm as the upper limit." Applicants respectfully request reconsideration of the rejection in view of the following comments

"With respect to changing numerical range limitations, the analysis must take into account which ranges one skilled in the art would consider inherently supported by the discussion in the original disclosure." See MPEP § 2163.05. For example, the Court of Customs and Patent Appeals held that a disclosure of a range of 25% to 60% solids content, which was supported by two examples that fell within that range, was sufficient support for a claim to a range of 35% to 60%. In re Wertheim, 191 USPQ 90, 98 (C.C.P.A., 1976). The court further held that: "Inventions are constantly made which turn out to be patentable, and applicants frequently discover during the course of prosecution that only a part of what they invented and originally claimed is patentable. . . . To rule otherwise would let form triumph over substance, substantially eliminating the right of an applicant to retreat to an otherwise patentable species merely because he erroneously thought he was first with the genus when he filed." Id. at 97. "The burden of showing that the claimed invention is not described in the specification rests on the PTO in the first instance, and it is up to the PTO to give reasons why a description not in *ipsis verbis* is insufficient." Id.

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Applicants' specification discloses that the collection of particles generally has an average particle size "preferably from about 5 nm to about 500 nm, more preferably from about 5 nm to about 100 nm, and even more preferably from about 5 nm to about 50 nm." See specification, for example, at page 17, lines 11-16. Additionally, the specification discloses a specific example where the collection of particles has an average particle size of about 20 nm. See Applicants' specification, for example, at Fig. 3. Thus, Applicants submit that one of ordinary skill in the art would, based upon the disclosed particle size ranges and specific example, consider the upper particle size limits of 25 nm, 125 nm and 150 nm inherently supported by the original disclosure. Additionally, Applicants submit that the Examiner has not met their burden of showing that Applicants' specification is insufficient to support the claimed upper particle size limits and that the Examiner has not presented a prima facie case for lack of written description.

Since Applicants' disclosure adequately supports upper particle size limits of 25 nm, 125, nm and 150 nm, Applicants respectfully request withdrawal of the rejections under 35 U.S.C. § 112, first paragraph, as containing subject matter which was not described in the specification.

Rejections Under U.S. Patent 5,840,111

In the Office Action of May 21, 2003, the Examiner rejected claims 22 and 29 under 35 U.S.C. § 102(b) as being anticipated by U.S. patent 5,840,111 to Wiederhoft et al. (the Wiederhoft patent). Applicants assume that the Examiner intended to reject claims 18-30 as being anticipated by the Wiederhoft patent to be consistent with the Office Action Summary and with rejections in previous Office Actions. Specifically, the Examiner asserted that "Wiederhoft teaches rutile titanium dioxide particles having a maximum value of the particle size distribution between 1 and 10 nm." In response to Applicants' previous arguments, the Examiner pointed to EP 444,798 for support for the Wiederhoft patent producing rutile titanium dioxide. In order for

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a reference to anticipate an invention, the reference must disclose each claimed element. Applicants submit that the Wiederhoft patent fails to disclose submicron titanium dioxide particles as described and claimed by Applicants, and therefore the Wiederhoft patent does not prima facie anticipate Applicants' claimed invention. Applicants respectfully request reconsideration of the rejection in view of the following comments.

The Wiederhoft patent discloses titanium dioxide solutions or sols, which generally comprise aqueous mixtures of precipitates, alcohols and hydroxide ions. See the Wiederhoft patent at column 3, lines 24-31. In particular, the titanium in the sols generally exists as an hydroxide rather than an oxide, and thus the sols must be dried in order to produce titanium dioxide. The Wiederhoft patent does not disclose drying the sols to form titanium dioxide. The dried materials form agglomerates. European Patent Application 444,798, which is referenced in the Wiederhoft patent, discloses that compounds made by the sulphate process have to be ground after drying to yield non-agglomerated particles. See EP 444,798 at page 5, lines 10-12. A copy of the EP 444,798 reference is attached for the Examiner's convenience. Thus, the dried products produced by the sulfate method are agglomerated masses, not particles, which have to be milled in order to produce non-agglomerated particles. Therefore, the Wiederhoft patent does not disclose submicron titanium oxide particles because the Wiederhoft patent generally only discloses aqueous sols, and the products that result from drying the sols are agglomerated masses. In contrast, Applicants' invention, as claimed in independent 18, relates to a "collection of nanoparticles, the nanoparticles comprising rutile titanium dioxide." Applicants use the term particles to include generally un-agglomerated forms of titanium dioxide. See throughout Applicants' specification. Since the Wiederhoft patent fails to disclose un-agglomerated submicron rutile titanium dioxide particles, the Wiederhoft patent does not prima facie anticipate Applicants' claimed invention.

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Since the Wiederhoft patent does not anticipate Applicants' claimed invention, Applicants respectfully request withdrawal of the rejection under 35 U.S.C. § 102(b) as being anticipated by the Wiederhoft patent.

Rejections Under U.S. Patent 3,923,968

The Examiner rejected claims 22 and 29 under 35 U.S.C. § 102(b) as being anticipated by U.S. patent 3,923,968 to Basque et al. (the Basque patent). Applicants are confused by the rejected claims since the corresponding independent claim was not included in the rejection. Applicants respectfully request clarification. With respect to the rejection, the Examiner asserted that the Basque patent discloses "rutile titanium dioxide particles having an effective diameter of not larger than 100 nm, in particular a diameter range of from 10 to 100 nm." Applicants submit that the Basque patent fails to disclose a collection of particles with the claimed uniform particles distribution. Therefore, the Basque patent does not anticipate Applicants' claimed invention. Applicants respectfully request reconsideration of the rejection in view of the following comments.

In order for a reference to anticipate an invention, the reference must disclose each claimed element. While the Basque patent is generally directed towards a method of preparing titanium dioxide pigment, the Basque patent does not disclose a collection of nanoparticles comprising rutile titanium dioxide wherein effectively no particle has a diameter greater than about four times the average diameter. In contrast, Applicants' invention, as claimed in independent claim 18, relates to a collection of nanoparticles comprising rutile titanium dioxide wherein "effectively no particles have a diameter greater than about four times the average diameter. Since the Basque patent fails to disclose this feature of Applicants' claimed invention, the Basque patent does not prima facie anticipate Applicants' invention.

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Since the Basque patent does not anticipate Applicants' claimed invention, Applicants respectfully request the withdrawal of the rejection under 35 U.S.C. § 102(b) as being anticipated by the Basque patent.

CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,



Peter S. Dardi, Ph.D.
Registration No. 39,650

Customer No. 24113
Patterson, Thuent, Skaar & Christensen, P.A.
4800 IDS Center
80 South 8th Street
Minneapolis, Minnesota 55402-2100
Telephone: (612) 349-5746



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(71) Applicant: KEMIRA OY
Porkkalankatu 3
SF-00180 Helsinki(FI)

(72) Inventor: Karvinen, Salla
Kuusamäke 37
SF-28660 Pori(FI)

(74) Representative: Pacitti, Pierpaolo A.M.E. et al
Murgltroyd and Company Mitchell House 333
Bath Street
Glasgow G2 4ER Scotland(GB)

(54) A new method of preparing titanium dioxide.

(57) The invention relates to a method of preparing microcrystalline titanium dioxide, in which

- a) the solid titanium dioxide hydrate is treated with a base,
- b) the precipitate treated with the base is treated with hydrochloric acid, and
- c) the precipitate treated with the base and the hydrochloric acid is neutralized.

It has been noted that usable rutile crystals, a more appropriate crystal size and crystal size distribution and that chemicals can be saved if as the final hydrochloric acid content of the stage a) is adjusted a lower value than usually, being about 8 to 25g/liter, for the precipitation of microcrystalline titanium dioxide. Hereby the neutralization of the stage c) can also be carried out by raising the pH to a higher value than usually, i.e. the value about 4.0 to 6.0.

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The invention relates to a new method of preparing microcrystalline titanium dioxide, having the crystal size <100nm, in which

- a) the solid titanium dioxide hydrate is treated with a base,
- b) the precipitate treated with the base is treated with hydrochloric acid, and
- 5 c) the precipitate treated with the base and the hydrochloric acid is neutralized.

The properties of the microcrystalline titanium dioxide differ from the properties of the usual titanium dioxide known as white pigment. The differences are due to the dissimilarities in the crystal size, for the crystal size of the microcrystalline titanium dioxide (10-100nm) is about 5 to 10 times smaller than the crystal size of the normal titanium dioxide (160 to 250nm). The crystal size becoming smaller the coverage
10 of titanium dioxide in the range of visible light disappears and the pigment becomes transparent. On the other hand, the permeability of UV-light decreases. Accordingly, the microcrystalline titanium dioxide is suitable for a UV-protective agent. Thanks to the small crystal size and the great specific surface titanium dioxide can be used as an effect pigment among other things in catalysts, ceramics and paints.

The preparation of microcrystalline titanium dioxide needs a process of its own in which the difficulty
15 lies in the creation, controlling and retaining of the small particle size throughout the process. The control of the purity and the crystal size distribution are important factors when assessing the various methods of preparation. Moreover, the preparation processes must be economically profitable and ecologically beneficial. Different crystal forms can be achieved by different methods. Rutile is known as a durable crystal form and its permeability to UV-light is less than that of anatase.

20 It is possible to prepare microcrystalline titanium dioxide by many different methods either by gas phase or by precipitating technique.

The titanium source or the titanium containing material can be e.g. titanium tetrachloride, titanium
alcooxide or titanium hydrate prepared from ilmenite. For the preparation of rutile precipitation methods have
been patented. In the JP patent 86/049250 a method of preparing microcrystalline titanium dioxide,
25 after-treated with aluminum and/or silicon dioxide, from titanium hydrate prepared from ilmenite and ammonia has been briefly presented. By using ammonia the bringing of foreign metal cations into the pigment is avoided but, on the other hand, you are compelled to handle troublesome ammonia reagent. The crystal form of the product is not mentioned in the patent specification, but it is not necessarily rutile. In a later application JP 57/87681 of the same Japanese applicant a similar method of preparation is presented
30 by which finely-divided anatase is created. Rutile is prepared in the same patent with a recipe starting from titanium tetrachloride. The neutralization is carried out with NaOH and water additions. The precipitation concentration is 30g/liter TiO_2 .

In DE 3817909 preparation of microcrystalline titanium dioxide both from ilmenite and titanium
tetrachloride is presented. The titanium hydrate mass prepared from ilmenite is treated with sodium
35 hydroxide to a titanium hydrate cake containing sodium. The pH is first set to the value 2.8 to 3.0 with a hydrochloric acid addition and at a later stage of the cooking the ratio between the acid and the titanium dioxide is adjusted to the value 0.26. At the end of the cooking the slurry is neutralized to the pH-value 7.5, after which the titanium dioxide is filtered and washed. Then the pigment is sand ground and after-treated
40 with aluminum and/or silicon dioxide. The crystals of the microcrystalline titanium prepared in this way become acicular. A drawback of the method is hereby for many purposes e.g. that the pigment is not calcinated, whereby the crystals would become rounder and the crystal size could be regulated. A further drawback of this known method is that the hydrochloric acid amount which is added to create the rutile crystals is dependent on the titanium dioxide concentration.

The wash of the titanium dioxide so as to become free from the precipitation salts is rather laborious, as
45 the final neutralization is carried out to the pH-value 7.

The same drawbacks also apply for the preparation of microcrystalline titanium dioxide from titanium tetrachloride presented in the same DE application.

In the USA patent specification 962,142 a very similar method of preparation is disclosed as in the
above-mentioned DE publication in which the starting material is ilmenite but after the neutralization of the
50 precipitation (with ammonia to the pH-value 6.5) the composition is cooked before the filtration and the wash and the so-called calcination chemicals (K_2O , P_2O_5) are added and the titanium dioxide is calcinated. This method does not any longer produce titanium dioxide which is sufficiently microcrystalline, but the crystal size achieved is 50 to 150nm.

In the method presented in the JP patent application 59223231, in which the starting material is titanium
55 hydrate mass, acicular rutile crystals are produced, which are coated with organic aluminum compounds. The titanium dioxide is not calcinated, for which reason the regulating of the crystal size is troublesome. The filtration difficulties are overcome by means of an organic after-treatment. Hereby, however, no conventional inorganic treatment recipes of titanium dioxide can be applied.

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In the corresponding method of preparation starting from the titanium hydrate mass the JP publication 62/235215 suggests solving the filtration and drying problem by means of a filtration film of 100Å and freezing drying. The method is troublesome, apt to disturbances and unnecessarily expensive.

An aim of the present invention is to prepare microcrystalline titanium dioxide particles in rutile crystal form, form a crystal size and crystal size distribution of the product as advantageous as possible, use as cheap and easily handled chemicals and devices as possible and to save as much process chemicals as possible.

The above-mentioned aims have been reached in the present invention by means of the four-phase method mentioned, which is mainly characterized in that the base treatment of the stage a) is carried out to an alkaline pH-value and to the final hydrochloric acid content is adjusted 8 to 25g/liter for the precipitation of the rutile-formed titanium dioxide.

Accordingly, the invention differs at least in two points from the prior art.

Firstly, it has been noted that rutile crystals are produced in a solution in which the measured HCl-concentration is about 8 to 25 g/liter independent of the concentration of the titanium dioxide. Accordingly, microcrystalline titanium dioxide having a more preferable crystal form is produced when a lower hydrochloric acid concentration than usual is used. Neither is a precise knowledge of the titanium dioxide concentration necessary any more, nor must the acid addition be increased as a function of the titanium dioxide concentration. At the same time chemicals are saved because greater consistencies thus also become possible.

Secondly, it has been noted that the pH-value of the final neutralization taking place in stage c) has a decisive effect on the filtrability of the precipitation mass and to its washing off of salts. The optimal pH-values of the final neutralization varying between about 4.0 to 6.0 were found and are thus lower than previously. As the hydrochloric acid used in the precipitation is neutralized in the very final neutralization stage mentioned it can be seen that also synergy occurs between the two steps mentioned as far as the quality of the product and the saving of chemicals are concerned. Accordingly, the invention is decisively helpful in the technical realization of the microcrystalline titanium dioxide and is very inexpensive.

In the first stage of the process according to the present invention the titanium-containing substance is in aqueous medium brought into contact with a first base.

The titanium-containing substance can be any titanium compound of a commercial process which is capable of precipitation and re-crystallization. According to a preferred embodiment it is a washed titanium dioxide hydrate precipitate obtained from a sulfate process, whereby it has been prepared by

- i) bringing ilmenite, its concentrate, or any other unpurified titanium dioxide raw-material to react with sulphuric acid,
- ii) dissolving the solid reaction product produced by means of water and e.g. waste acids of the process,
- iii) reducing and clarifying the dissolved reaction composition,
- iv) concentrating the solution obtained by dissolution from the reaction composition,
- v) precipitating the titanium containing substance from the solution by means of hydrolysis, and
- vi) washing the precipitation mass obtained in stage a) for the use as a titanium containing substance.

When the titanium containing substance is this kind of an intermediate product of a sulfate process the method is preferably carried out in the following manner:

The solid titanium dioxide hydrate is treated with the first base, preferably with an aqueous solution of sodium hydroxide at an elevated temperature, after which the obtained titanium mass treated in base is washed, preferably hot, filtered and elutriated again. Then the temperature of the slurry is raised to about 60° C. Hereby, it is preferable that before the raise of temperature the pH is adjusted by hydrochloric acid to the value of about 1.5 to 2.0, and preferably to the value about 1.8. Finally, the concentration of the hydrochloric acid is adjusted to the mentioned final hydrochloric acid content of the stage b) for the precipitation of the microcrystalline titanium dioxide.

Hereby it is advantageous that the base treatment i.e. the stage a) is carried out at the temperature of about 95° C. The base treatment of the stage a) is preferably carried out so that the base concentration correspond to about 300 to 350g NaOH/liter of H₂O.

The concentration of the stage b) is in the beginning preferably about 95 to 180g/liter. As has been stated above about 8 to 25g/liter has been adjusted as the final hydrochloric acid content of the stage a). It is more preferable to adjust the content to the value 8 to 15g/liter and most preferable to adjust it to the value 8 to 12g/liter i.e. about 10g/liter.

After the final hydrochloric acid content of the stage b) mentioned has been adjusted, the composition is preferably still heated before the neutralization of the stage c). When washed titanium dioxide hydrate precipitate obtained from the sulfate process is used the heating preferably comprises a slow heating to the boiling point and cooking for about two hours. The precipitate to be treated is at the stage b) in the form of

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slurry, the content of which is at least 70g/liter, preferably 70 to 180g/liter.

The neutralization of the composition obtained from the stage b) is carried out in stage c). The neutralization is carried out by raising the pH to the value above about 4.0, but below about 6.0 and preferably to the value about 4.4 to 5.0. The neutralization is preferably carried out with sodium hydroxide or sodium carbonate.

After the neutralization of the stage c) the reaction composition is optionally treated further in stage d). After the stage c) a filtration and wash of the microcrystalline titanium dioxide precipitate is almost always carried out. When, according to the present invention the neutralization is carried out cautiously to the pH-value below 6 and still more preferably below 5, the filtration and wash succeeds particularly well and almost all sodium and chloride ions affecting detrimentally the further treatment of the product can be removed from the precipitate.

When the filtration and wash stage is performed, the further treatment stage d) preferably comprises at least the calcination of the purified neutralized composition, preferably at the temperature 350 to 800 °C. Hereby it is particularly preferable to adjust the crystal size of the microcrystalline titanium dioxide by means of the calcination temperature. The crystal size and the crystal size distribution can be readily and precisely regulated by the calcination parameters of salt-free, rutile-formed titanium dioxide mass. The crystals of the calcinated pigment are ellipsoidal in form (oval).

The further treatment d) of the method according to the invention can also comprise stages which are similar to the aftertreatment stages of the usual titanium dioxide pigment. Hereby, similar dispersion and weather-resistance properties are achieved as with titanium dioxide pigment. The product obtained from the calcination can be rough-ground e.g. with a hammer grinder and finely ground e.g. by sand grinder.

After the grinding the microcrystalline titanium dioxide is treated with treatment recipes of titanium dioxide pigment in use so that the surface of titanium dioxide is coated with aluminum, silicon and/or zirconium oxide hydrate or oxide. On the surface of the pigment there might be from 0 to 10% of aluminum oxide, from 0 to 10% of silicon dioxide and zirconium oxide calculated as zirconium from 0 to 5%. The treated pigment is dried, before which it is treated with an organic auxiliary agent, such as e.g. trimethylolpropane or silicon (see FI patent specification 57124).

The microcrystalline TiO₂-pigment can finally be ground with an efficient mill. The finely-ground microcrystalline TiO₂-pigment treated with various coatings is suitable for use as effect pigments e.g. in car paints, as UV-A- and a UVB-protective agent in cosmetic, as UV-protective agent in timber protection or in packing plastics for foodstuffs to protect a UV-light sensitive foodstuff.

Example 1

The preparation of titanium dioxide by sulfate method is began by the ilmenite concentration reaction together with sulphuric acid. The created solid reaction cake is dissolved by means of water and waste acids. The impurities are removed and the iron sulfate is crystallized away. The titanium containing solution is concentrated and the titanium dioxide hydrate is precipitated by hydrolyzation. This precipitation mass is washed in several stages so as to become free of salts. 1400g of this washed filtration cake is elutriated with 1200ml of distilled water. The slurry is made strongly basic by adding at 60 °C 1070ml of NaOH-solution (70 g/liter). The temperature of the slurry is raised to 95 °C and the slurry is agitated for two hours at this temperature. After this the sulfate ions are removed from the titanium hydroxide mass by washing the slurry for so long with hot distilled water that no phosphates are found in the filtrates when precipitation is carried out with barium chloride.

The filtrate cake which is free from sulfates is elutriated into distilled water so that the concentration of the dispersion expressed as titanium dioxide is about 180g/liter. The pH of the slurry is set to 1.8 by adding 37% hydrochloric acid to the slurry. Continuously agitating the temperature of the slurry is raised to 60 °C. In this temperature the slurry is agitated for 30 minutes, after which acid content of the slurry is set to 10g HCl/liter by an addition of 37% hydrochloric acid for the formation of rutile formed crystals. The temperature of this dispersion is raised slowly under constant agitation to 90 °C. The slurry is cooked under agitation at this temperature for 120 minutes.

Finally, the slurry is neutralized with sodium carbonate or sodium hydroxide so that the pH settles at 4.7 to 4.8. If the neutralization result is more basic the washing off of the sodium ions becomes more difficult and if the neutralization result is more acidic the washing off of the chloride ions becomes more difficult. The neutralized slurry is filtered and washed with (4 liters of) distilled water. The dry content of the filtrate cake is about 30%. An X-ray diffraction diagram was taken of the dried filtrate cake and the microcrystalline titanium dioxide is found to be of rutile crystal form.

The titanium dioxide filtrate cake is calcinated at a temperature of 500 °C for one hour. As the average

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crystal size is measured about 25nm from the electron microscope picture of the calcinated rutile-formed product the distribution being from 10 to 50 nanometres. The sodium content of the calcinated product is below 0.1% and the chloride content below 0.05%. The electron microscope picture of the created product is presented in the attachment 1 together with a crystal size distribution diagram.

5 The titanium dioxide free of salts is elutriated by means of dispersing agent into distilled water as a thick slurry. The grinding is carried out in a sand mill. The crystals ground apart from each other are after-treated according to the planned use with an aluminum, silicon and/or zirconium compound. As recipe is used known recipes for the treatment of titanium dioxide pigments, such as e.g. FI patent specification 62130.

10 The treated microcrystalline TiO_2 is dried. Before drying organic agent, such as trimethylolmethane (TME) or silicone (see FI patent specification 57124). The dried microcrystalline TiO_2 is spray-ground into finely-divided powder having the particle size below 200nm.

Example 2

15 Microcrystalline titanium dioxide was precipitated and calcinated as in example 1, and the crystal size obtained was 25nm. The water dispersion of the calcinated microcrystalline titanium dioxide was ground in a sand mill as in example 1. The pigment slurry was diluted to a TiO_2 -content of 225g/liter and heated to the temperature 40°C. An amount corresponding to 0.5% of Al_2O_3 calculated on the TiO_2 of the slurry of acidic aluminum sulfate solution was added to the slurry. During this addition the pH of the slurry sank to the value 2.5. The slurry was neutralized with sodium carbonate solution to the value 6.4. After the neutralization the treated titanium dioxide pigment was recovered by filtering. The filtrate cake was washed with water from which the salts had been removed by means of an ion exchanger. 4% of dimethylpolysiloxane calculated on the TiO_2 was added to the washed filtrate cake. The pigment was washed and ground in a spray mill. The 25 particle size of the dried and spray-ground pigment was below 200nm. LDPE plastic films were prepared, to which different amounts of microcrystalline titanium dioxide was added. The thickness of the films was 25µm and the contents of microcrystalline titanium dioxide were 0, 0.5, 1.0, and 2.0%. The light and UV-radiation permeabilities of these films were measured. Appendix 2.

Example 3

30 A titanium hydrate mass according to example 1 treated with base, which had been washed and filtered, was elutriated in water so that the concentration of the dispersion expressed as titanium dioxide is about 180g/liter. The temperature of the slurry was raised to 60°C under constant agitation. The acid content of the slurry was set by an addition of 37% hydrochloric acid to 10g HCl/liter. The temperature of this dispersion is raised slowly under constant agitation to 90°C. The slurry is cooked at this temperature for 120 minutes.

40 The slurry is neutralized, filtered and washed as in example 1. The titanium dioxide filtrate cake is calcinated at the temperature of 500°C for one hour. The product produced is on the basis of an X-ray diffraction diagram rutile-formed microcrystalline titanium dioxide. Of the chemicals used in the preparation below 0.05% of sodium has remained in the titanium dioxide on the basis of atom absorption spectrophotometric determinations and below 0.15% of chloride on the basis of X-ray fluorescence determinations.

Example 4

45 The precipitated mass according to example 1 being under agitation is finally neutralized to the pH-value of 6.1. The slurry is washed and filtered as in example 1 and calcinated at the temperature of 500°C for one hour. In analysis with atom absorption spectrophotometer the Na-content of the pigment was found to be 7.1% and the Cl-content in X-ray fluorescence analysis 282 ppm. When this pigment is dispersed in water, as in example 1, the slurry thickens to a thick mass so its grinding to finely-divided particles becomes extremely difficult.

Example 5

50 The precipitated mass according to example 1 being under agitation is finally neutralized to the pH-value of 4.1. The slurry is washed and filtered as in example 1 and calcinated at the temperature of 500°C for one hour. In analysis with atom absorption spectrophotometer the Na-content of the pigment was found

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to be 0.01%, and the Cl-content in X-ray fluorescence analysis 0.23%. When this pigment is dispersed in water, as in example 1, the slurry thickens to a thick mass in the mill so that it cannot be ground as such in the sand mill. The only remaining means is to wash the salts off with a very abundant water wash after the calcination.

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Example 6

The filtrate cake free from sulfates prepared according to example 1 is elutriated into distilled water so that the concentration of the slurry expressed in titanium dioxide is about 95 to 100g/liter. The pH of the slurry is set to 1.8 by adding 37% hydrochloric acid to the slurry. Under constant agitation the temperature of the dispersion is raised to 60°C. At this temperature the solution is agitated for 30 minutes, after which the oxygen content of the slurry is set by a 37% hydrochloric acid addition to 9g HCl/liter so as to produce rutile-former crystals. The temperature of this slurry is raised slowly under constant agitation to 90°C. The slurry is cooked under agitation at this temperature for 120 minutes.

Finally, the slurry is neutralized as in example 1 to the pH-value 4.7 to 4.8 and washed as in example 1. The crystal form of the precipitated and dried product was checked by an X-ray diffraction method. It was found to be of rutile form. The crystal size is regulated by calcination parameters.

Example 7

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The filtrate cake free from sulfates prepared according to example 1 is elutriated into distilled water so that the concentration of the slurry expressed in titanium dioxide is about 140g/liter. The pH of the slurry is set to 1.8 by adding 37% hydrochloric acid to the slurry. Under constant agitation the temperature of the slurry is raised to 60°C. At this temperature the slurry is agitated for 30 minutes, after which the oxygen content of the slurry is set by a 37% hydrochloric acid addition to 10g HCl/liter so as to produce rutile-former crystals. The temperature of this slurry is raised slowly under constant agitation to 90°C. The slurry is cooked under agitation at this temperature for 120 minutes.

Finally, the slurry is neutralized as in example 1 to the pH-value 4.7 to 4.8 and washed as in example 1. The crystal form of the precipitated and dried product was checked by an X-ray diffraction method. It was found to be of rutile form.

Example 8

The filtrate cake free from sulfates prepared according to example 1 is elutriated into distilled water so that the concentration of the dispersion expressed in titanium dioxide is about 120g/liter. The pH of the slurry is set to 1.8 by adding 37% hydrochloric acid to the slurry. Under constant agitation the temperature of the slurry is raised to 60°C. At this temperature the slurry is agitated for 30 minutes, after which the oxygen content of the slurry is set by a 37% hydrochloric acid addition to 6g HCl/liter. The temperature of this slurry is raised slowly under constant agitation to 90°C. The slurry is cooked under agitation at this temperature for 120 minutes.

Finally, the slurry is neutralized as in example 1 to the pH-value 4.7 to 4.8 and washed as in example 1. The crystal form of the precipitated and dried product was checked by an X-ray diffraction method. It was found to be of anatase form. The titanium dioxide filtrate cake is calcinated at the temperature of 1000°C for one hour. In the calcination the product does not turn to rutile.

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Example 9

Precipitated and washed rutile-formed titanium dioxide is calcinated according to example 1 in various temperatures for one hour. The crystal size can be handily regulated by changing the calcination conditions, as appears from the electron microscope pictures.

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Table

	<u>Temperature</u>	<u>Crystal size</u>	<u>Top</u>	<u>Size distribution</u>
5	400°C	24nm	25nm (39%)	10-50nm
	500°C	26nm	25nm (37%)	10-50nm
	550°C	30nm	27nm (33%)	10-50nm
10	600°C	35nm	31nm (36%)	10-60nm
	650°C	45nm	40nm (25%)	10-70nm

15 Example 1:

As the starting materials of microcrystalline titanium dioxide is used a hydrochloric acid solution of titanium tetrachloride (200g/liter of TiO_2 and 345g/liter of HCl) and sodium carbonate solution (250g/liter Na_2CO_3). To a three-necked colonne of two liters is poured on the bottom 638ml of sodium carbonate solution and 12ml of distilled water. To the middle opening of the three-necked colonne is put a mixer and to the side openings a thermometer and a gauge tank of titanium tetrachloride. The mixer is started and the colonne is heated with a surrounding heating mantle to a temperature of about 40°C. To the colonne is dropped 350ml of titanium tetrachloride slowly from the gauge tank. The solution is agitated constantly but not heated. When all the titanium tetrachloride solution has been added the titanium dioxide content in the slurry is 9g/liter and the hydrochloric acid content 10g/liter. The temperature of the dispersion is raised slowly to 80°C. At this temperature the slurry is agitated for 30 minutes.

Finally, the slurry is neutralized with sodium hydroxide or sodium carbonate to the pH-value 11.5. In this pH the filtration and wash are carried out most successfully. The precipitated rutile-formed titanium dioxide is filtrated and washed with two liters of distilled water. The dry content of the washed and filtrated cake is about 30% and the measured Na-content below 0.1% and Cl-content below 0.05%.

The washed and filtrated cake is calcinated at the temperature of 500°C for one hour. Hereby the average crystal size will be about 25 nanometers and the distribution 20-50nm. The agglomerates formed in the calcination are ground in the sand mill. A thick water dispersion is prepared from the titanium dioxide by using an organic dispersion additive as an aid. The grinding succeeds very well because the titanium dioxide is as free as possible from the salts.

The crystals ground apart from each other are after-treated according to the planned use with aluminium, silicon or zirconium compounds. As the recipe is used known treatment recipes of titanium dioxide pigments, such as e.g. FI patent specification 62130 (1980).

The treated microcrystalline TiO_2 is dried. Before drying an organic material, such as trimethylethane (TME) or silicone, is added, see FI patent specification 57124 (1978). The dried microcrystalline TiO_2 is ground to finely-divided powder having the crystal size of below 200nm.

Example 1:

The water dispersion of the calcinated microcrystalline titanium dioxide was ground in a sand mill as in example 1. The pigment slurry was diluted to the TiO_2 -content 225g/liter. The pigment slurry was heated to 40°C. To the slurry was added solution containing aluminium in an amount corresponding to 4.5% of Al_2O_3 calculated on the TiO_2 of the slurry and solution containing zirconium in 0.7% calculated on the TiO_2 . After this a solution containing silicon was added to the solution to 2.2% of SiO_2 calculated on the TiO_2 and the mixture was agitated. After neutralization the treated titanium dioxide pigment was recovered by filtration. The filtrate cake was washed with water, from which the salts had been removed by the aid of an ion exchanger. Trimethylethane was added to the washed filtrate cake and it was dried and finally ground in a spray mill. The particle size of the dried and spray-ground pigment was below 200nm. The coating contents of the TiO_2 analyzed from the end product were 4.0% of Al_2O_3 , 2.2% of SiO_2 , 0.4% of Zr, 0.7% of C.

Example 1:

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A mass under agitation according to example 10 precipitated from titanium tetrachloride solution and sodium carbonate solution is finally neutralized to the pH-value 6.0. The slurry is washed and filtrated as in example 10 and calcinated at the temperature of 500 °C for one hour. In the analysis the Na-content of the pigment is 0.9%. When this pigment is dispersed into water as in example 10, the slurry becomes thick.

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Example 11

A mass under agitation according to example 10 precipitated from titanium tetrachloride solution and sodium carbonate solution is finally neutralized to the pH-value 3.0. The slurry is washed and filtrated as in example 8, but the filtration does not succeed but the slurry penetrates the cloth of the filter.

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Example 12

Rutile-formed titanium dioxide precipitated and washed according to example 10 is calcinated in various temperatures for one hour. The crystal size can be handily regulated by changing the calcination conditions.

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Table

<u>Temperature</u>	<u>Crystal size</u>	<u>Top</u>	<u>Size distribution</u>
400 °C	22nm	22nm (42%)	10-40nm
500 °C	25nm	23nm (40%)	10-45nm
550 °C	26nm	26nm (35%)	10-50nm
600 °C	30nm	31nm (30%)	10-50nm
700 °C	42nm	32nm (24%)	10-60nm

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Claims

- Method of preparing microcrystalline titanium dioxide, having the crystal size <100nm, in which:
 - the solid titanium dioxide hydrate is treated with a base,
 - the precipitate treated with the base is treated with hydrochloric acid, and
 - the precipitate treated with the base and the hydrochloric acid is neutralized, characterized in that the base treatment of the stage a) is carried out to an alkaline pH-value and the final hydrochloric acid content is adjusted 8 to 25g/liter for the precipitation of the microcrystalline titanium dioxide.
- Method according to Claim 1, characterized in that the neutralization of the stage c) is carried out to a pH-value of about 4.0 to 6.0.
- Method according to Claim 1 or 2, characterized in that the titanium dioxide hydrate is prepared from unpurified titanium dioxide raw-material by a sulfate process i.e. by means of sulphuric acid treatment, dissolution, separation and hydrolytic precipitation.
- Method according to any of the claims 1, 2 or 3, characterized in that the precipitation treated with base is at the stage b) in the form of slurry having the content of at least 70g/liter, preferably 70 to 180g/L.
- Method according to any of the preceding claims, characterized in that the treatment of the stage a) is carried out so that the base concentration corresponds to a size class of about 300 to 350g NaOH/liter of H₂O.
- Method according to any of the preceding claims, characterized in that the treatment of the stage a) is carried out with a base solution of sodium hydroxide at an elevated temperature.

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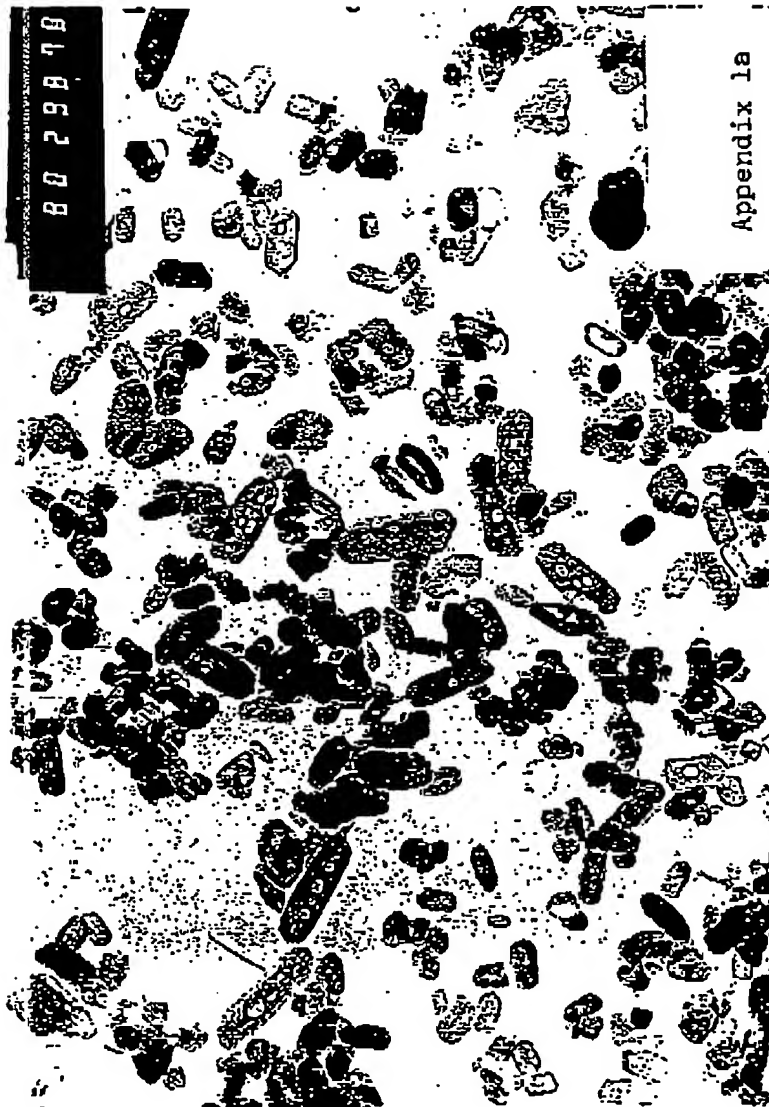
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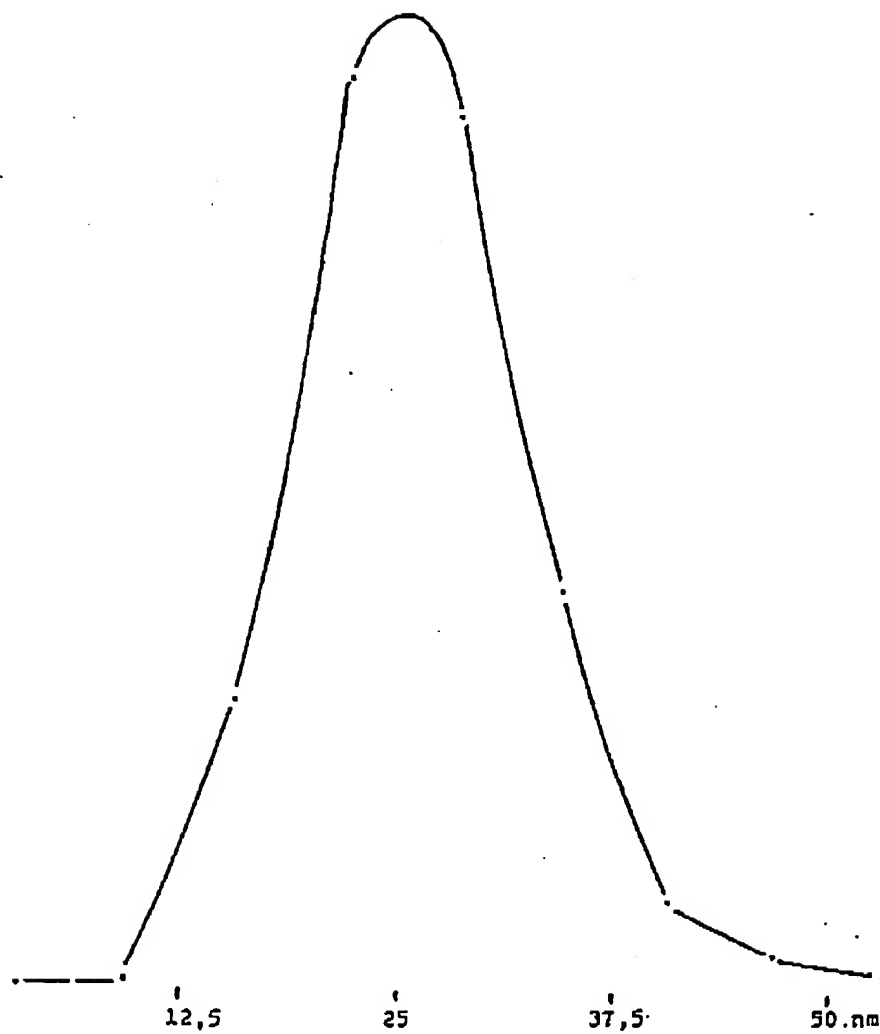
7. Method according to Claim 6, characterized in that the stage a) is carried out by adding the base solution at a temperature of about 60 °C, then raising the temperature for about 2 hours to about 85 °C, and washing with hot water.
8. Method according to any of the preceding claims, characterized in that the stage b) is carried out by precipitating the solid product obtained from the stage a) into water to form a slurry, by raising the temperature of the slurry to about 60 °C and then adjusting the concentration of the hydrochloric acid to the mentioned final sulphuric acid content of the stage b).
9. Method according to Claim 8, characterized in that the concentration of the slurry prepared in the beginning of the stage b) is about 95 to 180g/liter.
10. Method according to Claim 8 or 9, characterized in that before raising the temperature of the slurry to about 60 °C the pH of the slurry is by means of hydrochloric acid set to the value about 1.5 to 2.0.
11. Method according to Claim 8, 9, or 10, characterized in that to the mentioned pH-value of the slurry is set to about 1.8.
12. Method according to any of the preceding Claims, characterized in that in the stage b) 37% hydrochloric acid is used.
13. Method according to any of the preceding Claims, characterized in that to the final hydrochloric acid content of the stage b) is adjusted to about 8 to 12g/liter, preferably about 10g/liter.
14. Method according to any of the preceding Claims, characterized in that after the final hydrochloric acid content of the stage b) has been reached the temperature is raised to at least 80 °C and the slurry is cooked for about 120 minutes.
15. Method according to any of the preceding Claims, characterized in that the neutralization of the stage c) is carried out with sodium carbonate or sodium hydroxide, after which the product obtained is filtered and washed.
16. Method according to any of the preceding Claims, characterized in that it also comprises a stage d), in which the solid product of the stage c) is calcinated e.g. at a temperature of 350 to 800 °C.
17. Method according to Claim 13, characterized in that the crystal size of the microcrystalline titanium dioxide is adjusted by means of the calcination temperature.
18. Method according to any of the preceding Claims, characterized in that the further treating stage d) at least comprises any of the following:
- grinding,
 - treatment with aluminum and/or zirconium compound,
 - treatment with silicon-containing inorganic compounds,
 - treatment with sulphuric acid,
 - treatment with organic additives.
19. Use of the method according to any of the preceding claims for the preparation of a rutile-formed microcrystalline titanium dioxide.

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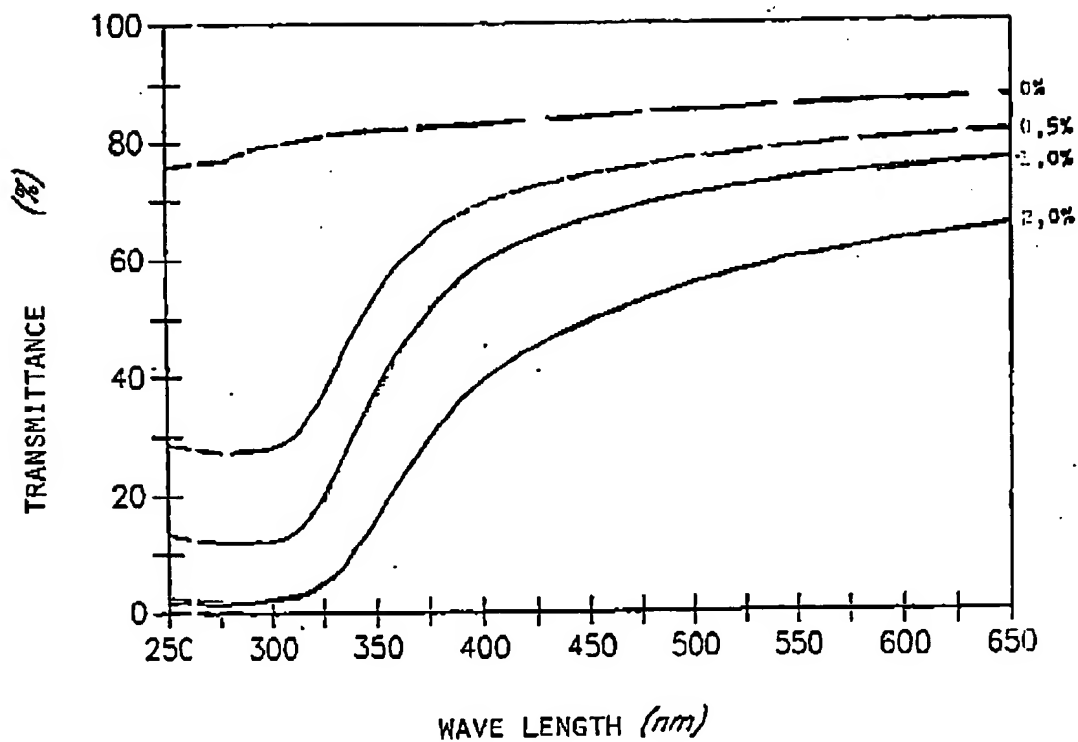
Appendix 1b

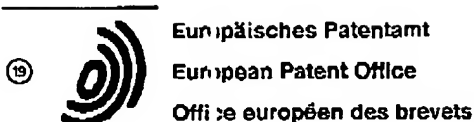


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Appendix 2

TRANSMISSION CURVES OF LDPE FILMS





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EUROPEAN PATENT APPLICATION

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71 Applicant: **KEMIRA OY**
Porkkalankatu 3
SF-00180 Helsinki (FI)

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72 Inventor: **Karvinen, Salla**
Kuusamatie 37
SF-28660 Pori (FI)

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70 Representative: **Pacitti, Pierpaolo A.M.E. et al**
Murgitroyd and Company Mitchell House 333
Bath Street
Glasgow G2 4ER Scotland (GB)

64 A new method of preparing titanium dioxide.

67 The invention relates to a method of preparing microcrystalline titanium dioxide, in which

- a) the solid titanium dioxide hydrate is treated with a base,
- b) the precipitate treated with the base is treated with hydrochloric acid, and
- c) the precipitate treated with the base and the hydrochloric acid is neutralized.

It has been noted that usable rutile crystals, a more appropriate crystal size and crystal size distribution and that chemicals can be saved if as the final hydrochloric acid content of the stage a) is adjusted a lower value than usually, being about 8 to 25g/liter, for the precipitation of microcrystalline titanium dioxide. Hereby the neutralization of the stage c) can also be carried out by raising the pH to a higher value than usually, i.e. the value about 4.0 to 6.0.

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European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 1183

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (INT. CL.5)
D,A	GB-A-2 205 083 (TIOXIDE GROUP PLC) "abstract; example 1"	1-15,18, 19	C 01 G 23/047
A	US-A-2 448 683 (J.H. PETERSON) "column 4, line 10 - line 45"	1-4,15, 16,19	
A	US-A-4 605 631 (G.A. ROSSI) "abstract"	1	
			TECHNICAL FIELDS SEARCHED (INT. CL.5)
			C 01 G C 09 C
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		05 December 91	REEDJK A.M.E.
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